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(24) Process for bleaching of lignocellulose-containing pulp.

(7) The present invention relates to a process for delignification and bleaching of chemically digested lignocellulose-containing pulp, wherein the pulp is acid treated at a pH of between about 1 and about 6, whereupon a water-soluble compound containing an alkaline earth metal is added at a pH of between about 1 and about 7 before the pulp is treated with a chlorine-free bleaching agent. The chlorine-free bleaching agent includes peroxide compounds, ozone, oxygen and sodium dithionite in an optional sequence or mixture. After the treatment according to the invention, the pulp may be finally bleached to the desired brightness, suitably with a chlorine-free bleaching agent, such as ozone, to completely avoid formation and discharge of AOX.

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The present invention relates to a process for delignification and bleaching of chemically digested lignocellulose-containing pulp, wherein the pulp is acid treated at a pH of between about 1 and about 6, whereupon a water-soluble compound containing an alkaline earth metal is added at a pH of between about 1 and about 7 before the pulp is treated with a chlorine-free bleaching agent. The initial acidic treatment removes the trace metals of the pulp, whereas the subsequent addition of alkaline earth metal ions in aqueous solution returns the ions to the positions in the pulp where they have a particularly beneficial effect on the preservation of the cellulose chains and, consequently, on the viscosity, as well as on the consumption of bleaching agent in the subsequent bleaching step. After the treatment according to the invention, the pulp may be finally bleached to the desired brightness, suitably with a chlorine-free bleaching agent, such as ozone, to completely avoid formation and discharge of AOX.

Background

In the production of chemical pulp of high brightness, wood chips are first cooked to separate the cellulose fibres. Part of the lignin holding the fibres together is thus degraded and modified, such that it can be removed by subsequent washing. However, in order to obtain sufficient brightness, more lignin has to be removed, together with brightness-impairing (chromophoric) groups. This is frequently effected by delignification with oxygen, followed by bleaching in several stages.

For environmental reasons, it has become increasingly common to treat chemical pulp with chlorine-free bleaching agents already in the first bleaching steps. The big advantage is the drastic reduction in the discharges of chlorinated organic substances detrimental to the environment, owing to the combined effect of a smaller amount of chlorine-containing bleaching agents and lower content of lignin, which is the organic substance primarily reacting with the chlorine.

It is known to use chlorine-free bleaching agents, such as hydrogen peroxide, peracetic acid or ozone, already in the prebleaching. However, the delignification and consumption of the bleaching agent become less effective than with chlorine-containing bleaching agents, unless the pulp is pretreated. Thus, a hydrogen peroxide treatment in an alkaline environment is disturbed by the presence in the pulp of ions of certain metals, such as Mn, Cu and Fe. These metal ions cause degradation of hydrogen peroxide, thereby reducing the efficiency of the peroxide treatment and increasing the consumption of peroxide. According to CA 1,206,704, this can be counteracted by pretreating the pulp with an acid, such as sulphuric acid or nitric acid, whereby the concentration of all types of metal ions is reduced. However, by this treatment also metal ions, for example Mg, which are advantageous to the peroxide treatment disappear, which ions stabilize the peroxide and increase the selectivity of the peroxide.

CA 575,636 discloses the addition of magnesium sulphate to stabilize alkaline peroxide solutions. However, the addition is made directly to the bleaching liquor and in alkaline environment insoluble magnesium hydroxide precipitates. Furthermore, US 4,222,819 discloses the addition of magnesium ions to acidic peroxide solutions, but also in this case the addition is made directly to the bleaching liquor. None of the related methods makes possible diffusion of the magnesium ions into the pulp to such an extent, that a pulp of high brightness and strength can be obtained.

The invention

The invention provides a process in which lignocellulose-containing pulp is treated under the conditions disclosed in the claims, whereby the metal ions harmful to the subsequent bleaching are effectively removed and the profile of alkaline earth metals is restored before the pulp is bleached in a chlorine-free bleaching step.

The invention relates to a process for bleaching of chemically digested lignocellulose-containing pulp, wherein the pulp is acid treated at a pH in the range from about 1 up to about 6, whereupon a compound containing an alkaline earth metal is added at a pH in the range from about 1 up to about 7 and in an amount of from about 0.01 kg, suitably 0.5 kg, up to about 10 kg/ton of dry pulp, calculated as alkaline earth metal, and that the pulp subsequently is treated with a chlorine-free bleaching agent.

Acid treatment is an effective process to eliminate metal ions from lignocellulose-containing pulps. At the same time it is known, that ions of alkaline earth metals, especially when in their original positions in the pulp, have a positive influence on the selectivity of the delignification as well as on the stability and consumption of chlorine-free bleaching agents, such as peroxides, ozone and oxygen. The present process presents an economic solution to the problem of creating a suitable trace-metal profile for the subsequent chlorine-free bleaching, in that non-desirable metal ions are eliminated while supplied ions of alkaline earth metals essentially recover the positions in the vicinity of the cellulose chains previously occupied by ions of

alkaline earth metals. This is achieved by adding the compound containing an alkaline earth metal at such a pH and such a temperature that the compound is dissolved in water, thus enabling the diffusion required to obtain the intended effect. Furthermore, an advantage of the present process is that the pH adjustment between the treatment with acid and addition of alkaline earth metal ions becomes very limited or may be left out altogether, which is advantageous to process technique and economy.

- 5 Chlorine-free bleaching agents include inorganic peroxide compounds, such as hydrogen peroxide and sodium peroxide, organic peroxide compounds, such as peracetic acid, as well as ozone, oxygen and sodium dithionite. Suitably, hydrogen peroxide (P), oxygen (O) and ozone (Z) are used in an optional sequence or mixture. Preferably, use is made of hydrogen peroxide or mixtures of hydrogen peroxide and oxygen (PO). The sequence P-Z or (PO)-Z are especially preferred.

- 10 In the treatment with a chlorine-free bleaching agent in an alkaline environment, pH is suitably adjusted by adding to the pulp an alkali or an alkali-containing liquid, such as sodium carbonate, sodium hydrogen carbonate, sodium hydroxide, oxidized white liquor or magnesium hydroxide slurry. Suitably, the magnesium hydroxide slurry is taken from the chemical handling system in the production of sulphite pulp with magnesium as base, i.e. magnesite pulp.

15 The acid treatment suitably is carried out with an acid. The acids used are inorganic acids, suitably sulphuric acid, nitric acid, hydrochloric acid or residual acid from a chlorine dioxide reactor, either separately or in an optional mixture. Preferably, sulphuric acid is employed.

- 20 Compounds containing an alkaline earth metal relate to water-soluble chemicals containing magnesium or calcium, or mixtures of such chemicals. Use is suitably made of magnesium-containing compounds, such as magnesium sulphate or magnesium chloride, or calcium-containing compounds, such as calcium chloride or calcium oxide. Use is preferably made of magnesium sulphate or magnesium chloride, the use of magnesium sulphate being especially preferred. The combination of temperature and pH at the addition of the compound containing an alkaline earth metal is always so chosen that the compound is in aqueous solution when contacted with the pulp.

- 25 In the process according to the invention, the acid treatment is carried out at a pH of from about 1 up to about 6, suitably from 1.5 up to 5, preferably from 2 up to 4. It is especially preferred that the acid treatment is carried out at a pH of from 2 up to 3. When magnesium is the alkaline earth metal in the compound containing an alkaline earth metal, the addition is made at a pH in the range from about 1 up to about 7, suitably in the range from 2 up to 6, preferably in the range from 2 up to 4. It is especially preferred that the addition of magnesium is made at a pH of from 2 up to 3. When the chlorine-free bleaching agent is hydrogen peroxide, the pulp is suitably treated at a pH of from about 8 up to about 12, preferably at a pH of from 10 up to 12. Treatment with the other chlorine-free bleaching agents mentioned above, is carried out within the normal pH ranges for each bleaching agent, which are well-known to the person skilled in the art.

35 The treatment according to the invention is preferably carried out with a washing step between the acid treatment and addition of alkaline earth metal ions, such that the trace metals that are harmful to the treatment with a chlorine-free bleaching agent are removed from the pulp suspension.

- 40 The realization of the acid treatment, a compound containing an alkaline earth metal and a chlorine-free bleaching agent, can be carried out at an optional position in the bleaching sequence, e.g. immediately after digestion of the pulp or after an oxygen step. The process according to the invention is preferably applied to pulp that has been delignified in an oxygen step prior to the treatment.

- 45 It is also within the scope of the invention, that the pulp in the acid treatment also can be subjected to bleaching and/or delignifying treatment. Bleaching and/or delignifying chemicals active within the pH range suitable in the acid treatment, are e.g. chlorine dioxide, ozone, peracetic acid and/or an acid peroxide-containing compound. Suitably, a combination of acid treatment and bleaching and/or delignifying treatment takes place in an ozone step.

- 50 Lignocellulose-containing pulps relate to chemical pulps of softwood and/or hardwood digested according to the sulphite, sulphate, soda or organosolv process, or modifications and/or combinations thereof. Use is suitably made of softwood and/or hardwood digested according to the sulphate process, preferably sulphate pulp of hardwood.

The treatment according to the invention can be applied to lignocellulose-containing pulps having an initial kappa number within the range from about 5 up to about 40, suitably 7 up to 32, preferably from 10 up to 20. Here, the kappa number is determined according to the standard method SCAN-C 1:77.

- 55 In the process according to the invention, the acid treatment is carried out at a temperature of from about 10 up to about 95°C, suitably from 20 up to 80°C and preferably from 40 up to 80°C, and for a period of time of from about 1 up to about 120 min, suitably from 10 up to 120 min and preferably from 20 up to 40 min. The compound containing an alkaline earth metal is added at a temperature of from about 10

95°C — 40-80
120 min — 10-120

10-95°C
1-120

up to about 95 °C, preferably from 40 up to 80 °C, and for a period of time of from about 1 up to about 180 min, preferably from 20 up to 180 min and preferably from 30 up to 120 min. When the chlorine-free bleaching agent is hydrogen peroxide, the pulp is treated at a temperature of from about 30 up to about 100 °C, preferably from 60 up to 90 °C, and for a period of time of from about 30 up to about 300 min, suitably from 60 up to 240 min. In the acid treatment and in the addition of alkaline earth metal ions, the pulp concentration may be from about 3 up to about 35% by weight, preferably from 3 up to 15% by weight. When the chlorine-free bleaching agent is hydrogen peroxide, the pulp concentration may be from about 3 up to about 50% by weight, suitably from 3 up to 35% by weight and preferably from 10 up to 25% by weight. Treatment with the other chlorine-free bleaching agents mentioned above, is carried out within the normal ranges of temperature, time and pulp concentration for each bleaching agent, which are well-known to the person skilled in the art.

The amount of compound containing an alkaline earth metal charged, lies in the range from about 0.01 up to about 10 kg/ton of dry pulp, calculated as alkaline earth metal, suitably in the range from 0.5 up to 5 kg/ton of dry pulp, calculated as alkaline earth metal, and preferably in the range from 2 up to 4 kg/ton of dry pulp, calculated as alkaline earth metal.

In preferred embodiments employing hydrogen peroxide as the chlorine-free bleaching agent, the amount of hydrogen peroxide, lies in the range from about 2 up to about 50 kg/ton of dry pulp, calculated as 100% hydrogen peroxide. The upper limit is not critical, but has been set for reasons of economy. The amount of hydrogen peroxide suitably lies in the range from 3 up to 30 kg/ton of dry pulp and preferably from 4 up to 20 kg/ton of dry pulp, calculated as 100% hydrogen peroxide.

After the acid treatment, a compound containing an alkaline earth metal and a chlorine-free bleaching agent, the pulp can be used for direct production of paper with a lower demand of brightness. Alternatively, the pulp may be finally bleached to the desired higher brightness, by treatment in one or more steps. Suitably, the final bleaching is also carried out with chlorine-free bleaching agents of the type mentioned above, optionally with intermediate alkaline extraction steps, which may be reinforced with peroxide and/or oxygen. In this way, the formation and discharge of AOX is completely eliminated. Suitably, the final bleaching is carried out with ozone in one or more steps. By the treatment according to the invention, the lignin content has been reduced to a sufficiently low level before any chlorine-containing bleaching agents are used. Therefore, chlorine dioxide and/or hypochlorite may well be used in one or more final bleaching steps without causing formation of large amounts of AOX.

Moreover, use of the process according to the invention means that the brightness and kappa number of the resulting pulp is higher and lower, respectively, than with the processes in which a compound containing an alkaline earth metal is not added at all or is added at a higher pH. In a process for bleaching chemical pulps, the aim is a high brightness as well as a low kappa number, the latter meaning a low content of undissolved lignin. At the same time, the consumption of the chlorine-free bleaching agent should be as low as possible meaning lower treatment costs. In the process according to the invention, these objects are met, as is apparent from the Examples. Furthermore, the strength of the pulp, measured as viscosity, is sufficient, which means that the pulp contains cellulose chains which are long enough to give a strong product.

The invention and its advantages are illustrated in more detail by the Examples below which, however, are only intended to illustrate the invention and are not intended to limit the same. The percentages and parts stated in the description, claims and examples, refer to percent by weight and parts by weight, respectively, unless anything else is stated.

Example 1

Sulphate pulp of softwood having a kappa number of 17, a brightness of 35% ISO and a viscosity of 970 dm³/kg was treated with sulphuric acid at a pH of 2.0. The pulp was treated at a temperature of 60 °C for 30 min, the pulp concentration being 10% by weight. After washing the pulp with water, magnesium was added in the form of an aqueous solution containing MgSO₄, to give a concentration of magnesium in the pulp of at least 500 ppm. In the tests, the pH at the time of the addition was varied between 2.3 and 11.5 by addition of sulphuric acid. Then, the pulp was bleached with hydrogen peroxide at a temperature of 90 °C, the residence time and pulp concentration being 180 min and 15% by weight, respectively. The final pH was 11.5, and the addition of hydrogen peroxide was 15 kg/ton of dry pulp, calculated as 100% hydrogen peroxide. For comparative purposes, magnesium was added directly to the hydrogen peroxide step under the conditions stated above, in accordance with the prior art. To provide a further comparison, the pulp was also treated with only sulphuric acid and hydrogen peroxide under the conditions stated above. The kappa number, viscosity and brightness of the pulp were determined according to SCAN Standard Methods, and

the consumption of hydrogen peroxide was determined by iodometric titration. The test results appear from the Table below.

TABLE I

pH at the addition of Mg	Kappa number step 2	Viscosity step 2 (dm ³ /kg)	Brightness step 2 (% ISO)	Residual H ₂ O step 2 (kg/ton)
2.3	9.1	903	61.0	1.5
4.7	9.2	910	60.0	1.0
9.5	9.8	930	56.1	0.9
11.5	10.0	940	52.2	0.2
---	9.8	890	54.1	0.5
2.3 -	9.9	875	48.2	0.0

* Magnesium added directly to the alkaline hydrogen peroxide step.

- No magnesium added.

As is apparent from the Table, the treatment according to the present invention with MgSO₄ at a pH in the range from about 2 up to about 6 is essential to give maximum increase in brightness and maximum reduction of the kappa number, as well as minimum decrease in viscosity and minimum consumption of hydrogen peroxide. Furthermore, the importance of the magnesium ions for the increase in brightness appears from the comparison at a pH of 2.3, where, in the final test, the peroxide treatment was preceded only by acidic treatment.

Example 2

Oxygen-delignified sulphate pulp of softwood having a kappa number of 13.7, a brightness of 37.1% ISO and a viscosity of 1057 dm³/kg, was treated in a first step with 15 kg of sulphuric acid/ton of dry pulp at a pH of 1.9. The pulp was treated at a temperature of 50 °C for 60 min, the pulp concentration being 10% by weight. After washing the pulp with water, in a second step between 0.1 and 1.5 kg of magnesium/ton of dry pulp was added in the form of an aqueous solution containing MgSO₄. Magnesium was added at a pH of 4.1, a temperature of 50 °C for 60 min and with a pulp concentration of 3.5% by weight. Then, the pulp was bleached with hydrogen peroxide at a temperature of 80 °C, the residence time and pulp concentration being 240 min and 10% by weight, respectively. The final pH was 11.5 and the addition of hydrogen peroxide was 20 kg/ton of dry pulp calculated as 100% hydrogen peroxide. For comparative purposes, the pulp was also treated with only sulphuric acid and hydrogen peroxide under the conditions stated above. The kappa number, viscosity and brightness were determined according to SCAN Standard Methods. The results after bleaching with hydrogen peroxide appear from the Table below.

TABLE II

Amount of Mg added in step 2 (kg/ton)	Amount of Mg in pulp after step 2 (ppm)	Kappa no. step 3	Viscosity step 3 (dm ³ /kg)	Brightness step 3 (% ISO)
0	3.7	9.6	900	51.5
0.1	130	8.2	870	61.8
0.3	250	7.8	864	65.1
0.75	370	7.7	855	65.9
1.5	480	7.6	845	67.3

As is apparent from the Table, acid treatment followed by addition of dissolved magnesium and bleaching with hydrogen peroxide according to the present invention, positively influence the pulp as regards kappa number, viscosity and brightness.

Example 3

The oxygen-delignified sulphate pulp of softwood used in Example 2, was treated in the sequences D -

EOP-Z - P (test 1) and D - EOP - Z - Mg - P (test 2), where the conditions in each step were equal in both sequences. D and EOP relate to a conventional chlorine dioxide step and a conventional alkaline extraction step reinforced with hydrogen peroxide and oxygen, respectively. Z relates to an ozone step with a pH of 2.3. Mg relates to the addition of 1 kg of magnesium/ton of dry pulp, in the form of an aqueous solution containing $MgSO_4$. Magnesium was added at a pH of 4.1, a temperature of 50 °C for 30 min, the pulp concentration being about 3% by weight. P relates to a hydrogen peroxide step, where the pulp was treated at a temperature of 80 °C for 120 min. The final pH was about 11.5 and the addition of hydrogen peroxide was 5 kg/ton of dry pulp calculated as 100% hydrogen peroxide. The viscosity and brightness were determined according to SCAN Standard Methods. The results after bleaching with hydrogen peroxide appear from the Table below.

TABLE III

Test	Amount of Mg added (kg/ton)	Amount of Mg in pulp after addition (ppm)	Viscosity (dm ³ /kg)	Brightness (% ISO)
1	0	18	820	86.3
2	1.0	255	872	88.4

As is apparent from the Table, addition of dissolved magnesium after an initial acid treatment with ozone and bleaching with hydrogen peroxide according to the present invention, positively influence the pulp as regards viscosity and brightness.

Example 4

The oxygen-delignified sulphate pulp of softwood used in Example 2, was treated in the sequences Step1 - P₁ - Z - P₂ (test 1) and Step1 - P₁ - Z - Mg - P₂ (test 2), where the conditions in each step were equal in both sequences. Step1 relates to treatment with CDTA at a pH of 5. Z relates to an ozone step with a pH of 2.3, the pulp concentration being 10% by weight. Mg relates to the addition of 1 kg of magnesium/ton of dry pulp, in the form of an aqueous solution containing $MgSO_4$. Magnesium was added at a pH of 4.1, a temperature of 50 °C for 30 min, the pulp concentration being about 3% by weight. P₂ relates to a hydrogen peroxide step, where the pulp was treated at a temperature of 80 °C for 120 min. The final pH was about 11.5 and the addition of hydrogen peroxide was 5 kg/ton of dry pulp calculated as 100% hydrogen peroxide. For comparative purposes, the pulp was also treated in the sequence Step1 - P₁ - Z - (PMg) (test 3). (PMg) relates to the addition of magnesium in the second alkaline hydrogen peroxide step under the conditions stated above, in accordance with the prior art. The viscosity and brightness were determined according to SCAN Standard Methods, and the consumption of hydrogen peroxide was determined by iodometric titration. The results after the second hydrogen peroxide step appear from the Table below.

TABLE IV

Test	Amount of Mg added (kg/ton)	Amount of Mg in pulp (ppm)	Viscosity (dm ³ /kg)	Bright-ness (% ISO)	H ₂ O ₂ consumed in P ₂ (% of added)
1	0	9	794	80.9	76
2	1.0	300	856	83.9	28
3	1.0	120	809	81.6	80

As is apparent from the Table, addition of magnesium within the present pH range before bleaching with hydrogen peroxide, positively influence the pulp as regards viscosity and brightness and reduces the consumption of hydrogen peroxide.

Claims

1. A process for delignification and bleaching of chemically digested lignocellulose-containing pulp, characterised in that the pulp is acid treated at a pH in the range from about 1 up to about 6.

whereupon a compound containing an alkaline earth metal is added at a pH in the range from about 1 up to about 7 and in an amount of from about 0.01 up to about 10 kg/ton of dry pulp, calculated as alkaline earth metal, and that the pulp subsequently is treated with a chlorine-free bleaching agent.

- 5 2. A process according to claim 1, characterised in that the chlorine-free bleaching agent consists of hydrogen peroxide, oxygen and ozone in an optional sequence or mixture.
3. A process according to claim 2, characterised in that the chlorine-free bleaching agent consists of hydrogen peroxide or a mixture of hydrogen peroxide and oxygen.
- 10 4. A process according to claim 1, characterised in that the compound containing an alkaline earth metal is added at a pH of from 2 up to 8.
- 15 5. A process according to claim 1, characterised in that the compound containing an alkaline earth metal consists of a water-soluble magnesium compound.
6. A process according to claim 1 or 5, characterised in that the compound containing an alkaline earth metal consists of magnesium sulphate or magnesium chloride.
- 20 7. A process according to claim 1, characterised in that the pulp is washed after the acid treatment.
8. A process according to claim 1, characterised in that the pulp, after the treatment, is finally bleached with a chlorine-free bleaching agent, optionally with intermediate alkaline extraction steps.
- 25 9. A process according to claim 8, characterised in that the pulp, after the treatment, is finally bleached with ozone in one or more steps.
- 30 10. A process according to claims 1-9, characterised in that the acid treatment is carried out at a temperature of from about 10 up to about 95° C for about 1 up to about 120 min, that the compound containing an alkaline earth metal is added at a temperature of from about 10 up to about 95° C for about 1 up to about 180 min and in an amount of from 0.5 up to 5 kg/ton of dry pulp, calculated as alkaline earth metal, the treated pulp having a concentration of from about 3 up to about 35% by weight, and that the pulp is treated with hydrogen peroxide at a pH of from about 8 up to about 12.

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OPTIMIZATION OF BLEACHING SEQUENCES USING PEROXIDE AS FIRST STAGE

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ABSTRACT

Hydrogen peroxide can delignify a kraft pulp as efficiently as oxygen does under conditions which are described.

It is shown that the efficacy of hydrogen peroxide as a delignifying agent depends on the pH of the liquor, on the amount of some metal ions and on the residual lignin structure in the unbleached pulp.

Interesting results are obtained when a hot (60-80°C) acid pretreatment is performed before an alkaline peroxide stage.

If the acid effect is combined with some chemical modifications of the residual lignin, like oxidation or nitration, delignification during the peroxide stage is dramatically improved.

INTRODUCTION

Hydrogen peroxide delignification of alkaline chemical pulps was proposed recently (1-5) and has been operating for two years on an industrial scale in an european mill (6).

Peroxide delignification offers some definite advantages over commercial oxygen delignification :

- it can be carried out at atmospheric pressure in a conventional equipment
- H_2O_2 is completely soluble in water and thus can be used very easily

However, H_2O_2 is relatively expensive and its real potential as a delignifying agent has not yet been studied extensively. One has to realize that the use of H_2O_2 to delignify a kraft (or a soda) pulp is quite a new development and that many studies have to be done to determine the effective reaction pathways and to find the best operating

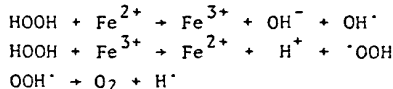
conditions. It is now well accepted (3,7) that the active delignification agents in alkaline medium are HO_2^- and the decomposition products of HO_2^- (radical species like OH^\cdot and O_2^\cdot , and oxygen). This indicates that the mechanism must be very complex and that all our knowledge in the field of H_2O_2 mechanical pulp bleaching is helpless to find the conditions appropriate to the delignification of a kraft pulp.

The aim of this paper is to define the main parameters of the H_2O_2 delignification treatment and to propose some improvements or modifications which allow it to match the conventional oxygen bleaching process.

RESULT AND DISCUSSION

Effect of metal ions

It has been described that in neutral or in acidic media the behavior of hydrogen peroxide may be completely modified by the presence of metal ions resulting in typical free-radical reactions. Thus ferrous or cuprous ions for example initiate the autocatalytic decomposition of H_2O_2 into water and oxygen. This is the Haber Weiss cycle :



But in the presence of a substrate RH which is susceptible to react with OH^\cdot radicals, other reactions can occur leading to substitution products like ROH. For example hydroxylation of phenolic compounds has been described (8). Similar reactions do occur in an alkaline medium and strongly affect the efficacy of H_2O_2 delignification as evidenced by the results given in tables 1 and 2.

Table 1. Effect of reducing the metal ion content of the pulp on H_2O_2 delignification (P) in alkaline medium.

	Metal ions content ppm				
	No Washing	Washing with H_2SO_4 0.72N	Washing with H_2SO_4 0.36N	Washing with H_2SO_4 0.10N	Washing with H_2SO_4 0.01N
Fe	53	26	30	30	31
Cu	8.8	3.0	3.0	4.0	4.0
Mn	103	< 0	< 0	< 0	10.0
Mg	540	180	200	250	270
Kappa No after P stage	20.5	16.9	16.9	17.0	17.4

Note P. stage conditions : consistency 12 %; NaOH 3 %; H_2O_2 1.5 %; 90° C ; 120 min.

Acid washing conditions : consistency 3 %, 20° C, 30 min.

Table 2. Effect of increasing the metal ion content of the pulp on H_2O_2 delignification (P) in alkaline medium

	Pulp washed with H_2SO_4 0.01 N							
	-	+ Mn 20 ppm	+ Mn 100 ppm	+ Cu 10 ppm	+ Cu 50 ppm	+ Fe 20 ppm	+ Fe 50 ppm	
Fe	31	31	31	31	31	51	81	
Cu	4.0	4.0	4.0	14.0	54.0	4.0	4.0	
Mn	10	30	110	10	10	10	10	
Mg	270	270	270	270	270	270	270	
Kappa No after P stage	17.4	20.0	21.0	18.0	18.8	18.4	18.7	

Note P stage conditions : consistency 12 % ; NaOH 3 % ; H_2O_2 1.5 % ; 90° C ; 120 min.

Acid washing conditions : consistency 3 % , 20° C , 30 min.

In these experiments the amount of metal ions have been reduced by submitting the softwood kraft pulp (kappa No 30) to an acid washing at room temperature and increased by adding some metal salts to the pulp after an acid washing. Mn can be removed completely by an acid washing, whereas Fe and Cu are only partly eliminated even in drastic conditions. At the same time the efficiency of H_2O_2 delignification is increased, suggesting that Mn is the most harmful catalyst. This is confirmed by the results on table 2 which indicate a clear dependence of the kappa number of the pulp after the P stage on the Mn content. Fe and Cu seem to slightly affect the delignification.

Effect of metal ions on peroxide consumption during H_2O_2 delignification was checked (Figure 1).

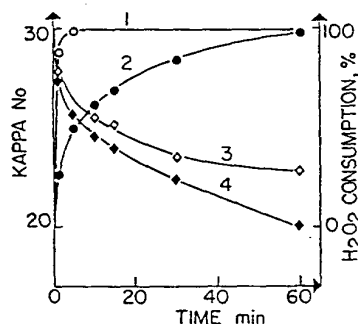


Fig. 1 Kinetics of H_2O_2 consumption (curves 1,2) and lignin solubilization (curves 3,4).

Conditions : consistency 12 % , NaOH 3 %
 H_2O_2 1 % , 90° C

Curves 1,3 without pretreatment
Curves 2,4 with acid pretreatment

H_2O_2 is consumed instantaneously during H_2O_2 delignification of the softwood kraft pulp (after 5 minutes of reaction time no H_2O_2 is detectable). However the kappa number is almost unchanged till about 100 % H_2O_2 has disappeared. After elimination of Mn and about half the original amount of Fe by acid washing the consumption of H_2O_2 is much slower and the kappa decrease faster. These results indicate that :

- HO_2^- reacts very slowly with the pulp
- Decomposition of HO_2^- is very quick when Mn is present (~ 100 ppm in our experiment)
- When large amounts of metal ions (particularly Mn) are present the mechanism for H_2O_2 delignification could be a rapid oxidation of the residual lignin by radical species or native O_2 followed by a slow alkaline extraction of the oxidized lignin. An other alternative could be a slow delignification of the pulp by O_2 liberated when the alkaline H_2O_2 solution is added to the pulp
- When the amount of metal ions is low (after acid washing) the mechanism of delignification could be the same as above except that here the formation of radical species or O_2 is slower. An other possibility could be a direct reaction of HO_2^- with carbonyl structures in residual lignin resulting in side-chain displacement (Dakin-like reaction) and possibly initiated by molecular oxygen and/or other peroxide decomposition products (7)
- Loss of delignification power when the pulp is rich in metal ions is due to intensive O_2 formation. O_2 solubility is too poor to recover all its oxidative power.

Effect of pH

It has been proposed to oxidize a kraft pulp by H_2O_2 in acidic medium (Pa) and to extract the oxidized lignin by an alkaline extraction treatment (E) (9). This sequence was investigated in this study along with other sequences consisting of acidic and alkaline peroxide steps. The main results are reported in Table 3.

Table 3. Comparison of acidic and alkaline peroxide treatments.

Treatment		Kappa No after the alkaline stage
1	2	
Alkaline H_2O_2 (P) H_2O_2 1 %	-	22.0
Acidic H_2O_2 (Pa) H_2O_2 1 %	alkaline extraction (E) H_2O_2 0	23.0
Acidic H_2O_2 (Pa) H_2O_2 0.5 %	alkaline H_2O_2 (P) H_2O_2 0.5 %	20.2
Acidic treatment (A) H_2O_2 0	alkaline H_2O_2 (P) H_2O_2 1 %	17.5

Note Acidic conditions : consistency 12 % ; H_2SO_4 2 % ; 90° C , 90 min.
Alkaline conditions : consistency 12 % ; NaOH 3 % ; 90° C , 90 min.

90°C 90 min

It is shown that although a PaE sequence is able to delignify a kraft pulp, the efficacy of the delignification is less than in a PaP sequence (at the same total H₂O₂ charge) where a part of H₂O₂ is introduced in the alkaline extraction step and much less than in an AP sequence, where all the H₂O₂ is added in the alkaline step. In other words H₂O₂ is much more efficient in an alkaline medium than in an acidic medium, as far as lignin splitting is concerned. So the best sequence seems to be an AP sequence where the alkaline peroxide step is preceded by a hot (70° C) acid pretreatment. These findings can be partly accounted for by the fact that O₂ (generated in acidic and alkaline medium as well) does not react with lignin in acidic medium as intensively as in alkaline medium. Another explanation could be that the reaction of OOH⁻ with carbonyl groups (Dakin-like reaction) is of particular importance as far as delignification is concerned.

Optimization of the acid pretreatment

Partial elimination of heavy metal ions can be achieved by acid treatment in gentle conditions (room temperature, pH ~ 2) and many acids can be utilized for that purpose as demonstrated in (10). Unexpectedly the data given in Table 4 clearly indicate that raising the temperature in the acid treatment results in a further decrease of kappa No after the P stage without altering more the metal ion content of the pulp, implying that kraft lignin is modified by an hot acid treatment so as to become more susceptible to solubilization in alkaline H₂O₂ liquor.

Table 4. Acid pretreatment prior to H₂O₂ delignification. Effect of temperature.

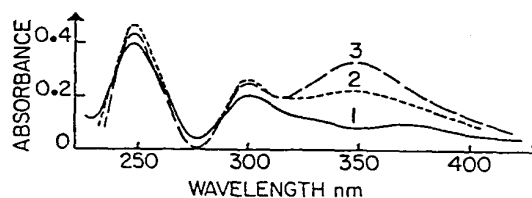
		No pretreatment	Acid pretreatment			
Temperature °C			20	50	70	90
Fe ppm	53		31	31	30	30
Cu ppm	8.8		4.0	3.7	3.8	4.0
Mn ppm	103		5.0	3.0	3.0	3.0
Kappa No after P stage	22.0		20.6	20.2	18.5	17.5

Note: Acid treatment conditions: consistency 12 %, H₂SO₄ 2 % (by weight of the dry pulp), 120 min.
P stage conditions: consistency 12 %, NaOH 1.5 %, H₂O₂ 1 %, 90° C, 90 min.

Thus, temperature of the acid liquor appears to be an important parameter. Acidolysis of kraft lignin has not been extensively investigated, so far. It is generally accepted that the number of hydrolysable ether linkages in kraft lignin is very low. However the curves in Figure 2 show that softwood

kraft lignin does react in dioxane water 9:1, HCl 0.2 N at temperature higher than 50° C, as evidenced by the new UV absorption maximum observed on the difference spectra of acidolysed lignin. The intensity of this 350 nm band decreases upon reduction with sodium borohydride indicating that a conjugated carbonyl group is formed during acidolysis. So the acidolysis results suggest that a significant amount of ether linkages (etherified units ?) are left unhydrolysed during kraft pulping and are cleaved by acidolysing the lignin. Consequently formation of carbonyl groups along with release of free phenolic group is achieved (12).

Figure 2. Acidolysis of softwood kraft lignin, dioxane-water 9:1, HCl 0.2N under reflux, 60 min. U.V. Difference spectra
1. reduced softwood kraft lignin
3. after acidolysis
2. after acidolysis and partial reduction. Na BH₄, 2 days



This is also confirmed by the slight increase of the maximum at 250 nm (despite the well known negative absorption of carbonyl groups at this wavelength), ascribed to free phenolic groups (11-12). Kinetics of the acidolysis reaction are given in Figure 3. At 40° C the reaction is very slow and is not detectable within the first four hours. After 4 hours at 60° C and 1 hour at reflux (~ 95° C) the acidolysis is almost completed.

Possibility of hydrolysis of some lignin carbohydrate linkages, thereby making the lignin more easily soluble in an alkaline medium, has to be considered as well, as suggested in (13).

Therefore there is a definite advantage to perform a hot acid pretreatment A prior to the alkaline peroxide stage P. Some technical aspects were then investigated like the effect of A on the strength properties and

bleachability of the pulp and on the waste-water loads.

Figure 3. Kraft lignin acidolysis. Variation of 350 nm maximum-UV difference spectra. dioxane-water 9:1
HCl 0.2 N

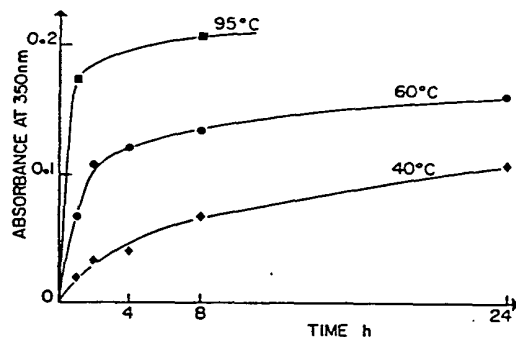


Table 5 shows that the main strength properties of the unbleached and AP treated pulps (A at 70° C) are somewhat comparable, in good accordance with the cellulose DP values which remain unchanged.

Table 5. Strength properties of AP treated pulps at 40° SR.

	Kappa number	DP of cellulose	Strength properties		
			Breaking length km	Burst index kPa m ² /g	Tear index mN m ² /g
Unbleached pulp	30	1150	9.75	7.22	9.03
AP treated pulp	18.5	1130	10.03	7.29	9.02

Note A conditions : consistency 12 % ; H₂SO₄ 2 % ; 70° C, 120 min
P conditions : consistency 12 % ; H₂O₂ 1 % ; NaOH 1.5 % , 90° C, 90 min

The excellent bleachability of AP treated pulps is demonstrated by the possibility of getting a fully bleached pulp by the short APDP sequence (Table 6). Effluent characteristics of A are given in Table 7. As expected from the value of the yield loss during the A pretreatment (about 0.3 % on pulp), the pollution loads are low. Color load is almost negligible and BOD₅ is about one tenth of the classical value

Table 6. Bleaching of softwood kraft pulps-Consumption of chemicals.

	A	P	D	P	Brightness
	H ₂ SO ₄ 2%	H ₂ O ₂ 1% NaOH 1.5 %	ClO ₂ 1.5%	H ₂ O ₂ 1.5% NaOH 1% H ₂ SiO ₃ 3% (31° 24)	87.5
C	Cl ₂ 6%	E	D	E	D
	NaOH 3%		ClO ₂ 1.2%	NaOH 1%	ClO ₂ 0.4%
					87.5

Table 7 : Effluent characteristics of bleaching sequences.

	Color kg/T	BOD ₅ kg O ₂ /T	COD kg O ₂ /T
CEDED	270	12.0	70.0
A	6.4	1.3	4.5
P	110	6.0	35.0
A P D P (AP recycled)	100	6.0	40.0

Note A: 70° C ; P: 1 % H₂O₂

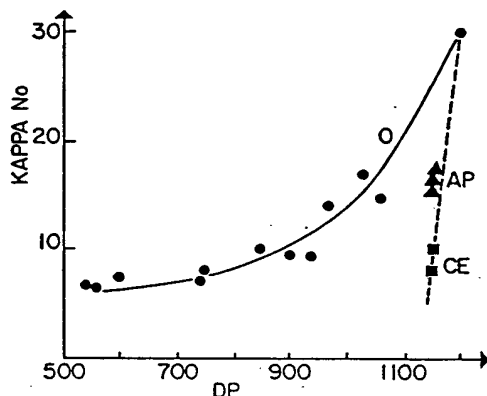
for a complete CEDED sequence. Therefore if any problem arises upon recycling the effluent (precipitation of dissolved lignin - release of H₂S) it should be possible to discharge it. Typically recycling the P effluent results in reduction of over 50 % in color 40 % BOD and COD when compared with CEDED. About 1 % H₂O₂ (by weight on dry pulp) is consumed.

Peroxide versus oxygen bleaching

It is well known that the selectivity of oxygen delignification is very bad even in the presence of cellulose protectors like magnesium salts ; as illustrated in Figure 4. DP of cellulose decreases dramatically with kappa No and consequently oxygen delignification must be stopped at a kappa No above 15 to preserve the strength properties of the pulp. From the selectivity point of view AP delignification is much better, since at kappa No 16 the DP value is almost unchanged, and matches the conventional CE sequence (Figure 4). Unfortunately for an unknown reason it has not been

possible to reach low kappa No with an AP sequence, even at high H_2O_2 charge. To equalize industrial oxygen bleaching in terms of delignification rate, 1 % to 1.5 % H_2O_2 must be consumed. Nevertheless peroxide bleaching should be considered due to its simplicity and low capital cost.

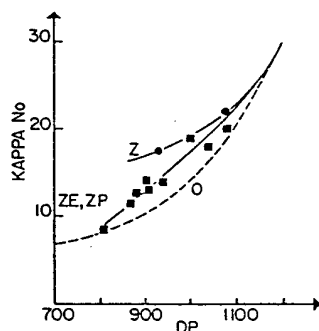
Figure 4 : Selectivity of Oxygen delignification. O conditions : Consistency 20 % pO_2 8 bars (at 20 °C) $MgSO_4$ 7H₂O 1%, NaOH 1%-5%, 90°C-120°C, 60 min



Combination of acid and chemical activation

Peroxide delignification can also be activated by a chemical pretreatment. Ozone (Z) oxidation of kraft pulps has been described by many authors (14). ZP sequence was investigated and compared to oxygen bleaching (figure 5).

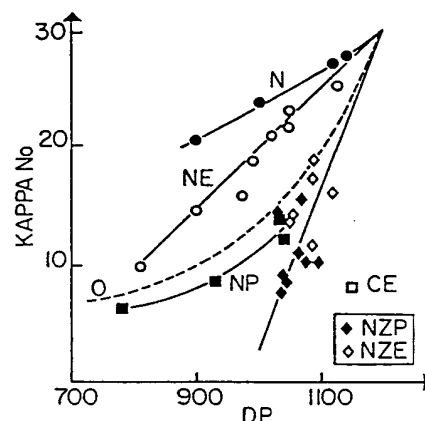
Figure 5. Selectivity of Z(ozone) ZE and ZP sequences. Z conditions : consistency 40%, O_3 1%-2%, 20 °C, 10 min. E/P conditions : consistency 12 %, NaOH 1%-3%, H_2O_2 0.5%-1% 80°C, 120 min



It is shown that low kappa No can be reached after ZP sequence but at the expense of cellulose DP so that ZP delignification is found less selective than O delignification. However it is demonstrated that ozone oxidation of lignin does not hinder the subsequent peroxide oxidation and can be associated with it to enhance the delignification.

Nitrogen dioxide (NO_2) activation has also been described in a previous paper (15) NO_2 pretreatment (N) allows peroxide delignification to be more performant and selective than oxygen delignification (Figure 6), although the difference is not very big. Thus lignin nitration can also be combined with peroxide oxidation to achieve a more complete delignification.

Figure 6 : Selectivity of N (nitrogen dioxide), NE, NP, NZE and NZP sequences. N conditions : consistency 40 %, NO 1%-6% 70 °C, 30 min, Other conditions as in Fig. 5

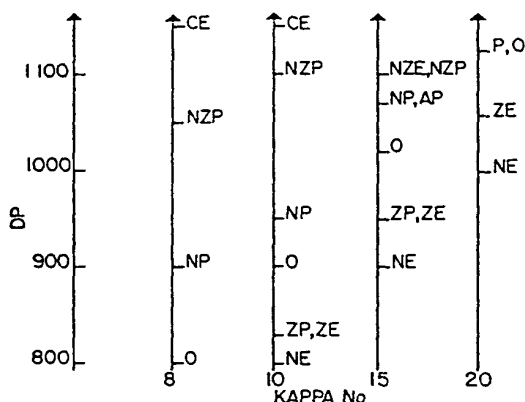


From these results, a novel, performant and chlorine free bleaching sequence was defined, combining all the effects we described in this study, i.e.

- hot acid effect (elimination of Mn cation and acidolysis of the residual lignin)
- lignin nitration
- lignin ozonization

NZP sequence was found to achieve this goal. Such a sequence is almost as efficient as CE bleaching, as indicated in Figure 6 and in Figure 7 where all the sequences under

Figure 7. Place of various sequences according to their selectivity



investigation are compared to one another at four different kappa levels. For example it has been possible to reduce the kappa No to 8.5 by applying NZP (NO_2 2%, O_3 1%, H_2O_2 0.5%, NaOH 2%). Whether or not it is interesting to introduce hydrogen peroxide in the alkaline treatment depends on economical factors and on the kappa target after treatment. NZE can be preferred to NZP to compete with the conventional oxygen bleaching. Kappa No 11.9 was obtained after NZE (NO_2 2%, O_3 1%, NaOH 2%). However only NZP sequence is able to approach the results of a CE treatment.

CONCLUSION

Peroxide delignification is a novel and promising development in the field of chemical pulp bleaching. The experiments carried out in this study show that:

- H_2O_2 in alkaline medium is much more active towards lignin than in acid medium
- The efficiency of H_2O_2 delignification in alkaline medium strongly depends on the content of metal cations, particularly Mn, in the pulp. An acid pretreatment performed at room temperature prior to H_2O_2 treatment eliminates most of the harmful cations thereby improving H_2O_2 delignification
- Unexpectedly if the acid treatment is carried out at higher temperature (60°C to 80°C), further improvement of H_2O_2 delignification is observed, whereas

cations removal is not better. It is suggested that lignin acidolysis takes place thereby breaking some residual ether linkages.

- Chemical modification of the residual lignin by nitration and/or oxidation in acid medium prior to alkaline H_2O_2 treatment dramatically improves the selectivity of the delignification. Some chlorine-free sequences are proposed which compete with conventional oxygen delignification.

EXPERIMENTAL

Pulp

Commercial unbleached softwood kraft pulp was used ("Obbola" scandinavian pulp). The pulp was in the form of dry sheets. The sheets were torn into small pieces by hand and disintegrated with water in a laboratory pulper.

Acid pretreatment

Acid treatments were performed in polyethylene (PE) bags - (for other conditions see tables 1, 2 and 4) after the desired retention time a sample of liquor was taken by squeezing the pulp and the pH was checked. The acid treated sample was cooled and the pulp was washed with cold tap water (50 ml/g of o.d pulp) and filtered to 30% consistency - Metal ions content was measured by atomic absorption spectroscopy. In some experiments Mn^{++} , Fe^{++} and Cu^{++} were added to the pulp after acid pretreatment. The corresponding sulfate salt was dissolved in water and an adequate volume of solution was added to the acid treated pulp, placed in a PE bag to 20% consistency. After thoroughly mixing (by hand) the pulp was left standing for 30 minutes at room temperature prior to subsequent peroxide treatment.

Peroxide treatment

H_2O_2 treatments were performed in PE bags which were collapsed to exclude as much air as possible (other conditions given in the text). In some experiments H_2O_2 was titrated during the treatment. The classical iodometric method was used (catalyst: ammonium molybdate)

Nitrogen dioxide and ozone treatments

NO_2 and ozone treatments were performed using a rotating round bottomed flask equipped with a gas inlet system. The pulp was fluffed at its designated mixture content by means of a mechanical fluffer and introduced into the flask.

The reaction flask and gas inlet systems were then partially evacuated by means of a mechanical vacuum pump to enable a weighed quantity of N_2O_4 to be introduced easily into the flask. Rotation of the flask was continued for the desired time with the

flask partially submerged in a water bath at constant temperature. After reaction the treated pulp was washed. Ozonization was carried out by treating the pulp with a stream of ozone in oxygen at ambient temperature. The gas velocity was adjusted so that during the resident time the desired quantity of ozone had been added onto the fibers. The exit gases from the reaction vessel were analysed for residual ozone content. After reaction the treated pulp was washed.

Other bleaching stages

C, D and E treatments were performed according to standard procedures (C : consistency 3.5 %, 45 min, room temperature ; D : consistency 6 %, 2 to 4 h, 70 °C ; E : consistency 8 %, 60 min, 60 °C).

Pulp and effluent characterization

Beating was carried out in a Jokro mill. Handsheets for physical testing were prepared at 70 g/m² and pulps were evaluated according to AFNOR methods (essentially the same as the TAPPI Testing Procedures) all other measurements were done according to the appropriate AFNOR standards.

Lignin acidolysis and lignin reduction

100 mg of softwood kraft lignin was dissolved in a mixture of 90 ml dioxane and 10 ml HCl 2N. After reacting for 1 h to 24 h the UV spectra of the lignin were recorded. 1 ml of reaction mixture was diluted with ethanol-water 50 : 50 (neutral solution). 1ml of reaction mixture was diluted with ethanol-water 50:50 NaOH 0.1N (alkaline solution). Borohydride reduction of lignin was carried out according to the classical method (16).

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ACID EXTRACTION OF THE ALKALINE WOOD PULPS
(KRAFT OR SODA/AQ) BEFORE OR DURING BLEACHING
REASON AND OPPORTUNITY

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ABSTRACT

The decreases in kappa number of an unbleached alkaline hardwood pulp of *carpinus berulus* when performing dilute H_2SO_4 hydrolysis at about $100^\circ C$, either after or before oxygen bleaching are the same. The main parameters of this acid hydrolysis are specified by studying the acidification of unbleached alkaline pulp suspensions at room temperature, and the extraction kinetics at temperatures in the range of $88^\circ-110^\circ C$ by following UV absorbance of the hydrolysis liquors.

Among the dissolved products in the liquors 2-furancarboxylic acid has been identified. This acid results probably from the degradation in the acid medium of compounds present in the unbleached alkaline pulp, which are not oxidized by oxygen in the alkaline medium.

INTRODUCTION

In view of decreasing, or indeed eliminating the production of toxic chlorinated organic materials^{1,2} during bleaching with chlorine, various methods are used or are now considered. One approach is the partial replacement of chlorine by chlorine dioxide in the C-stage³; another is to extend the cooking time⁴ or to use the "rapid displacement heating" pulping system⁵, in order to reduce the chlorine demand of the pulp by lowering the kappa number prior to bleaching.

Acid
 $88-110^\circ C$

A - O
 $88-110^\circ C$
A - P

O - A

MARÉCHAL

A more satisfactory solution would be the use of oxygen (or hydrogen peroxide) instead of chlorine; unfortunately the treatment of the pulp with oxygen in the alkaline medium is limited by the existence of a "limit kappa number" beyond which it is not possible to further delignify without degradation of polysaccharides⁶. The numerous investigations carried out to solve this problem do not propose any satisfactory solution, but allowed the industrial development of oxygen bleaching⁷ owing to the discovery of a carbonylhydrate protector⁸: Mg^{2+} . However, the efficiency of magnesium in preserving pulp viscosity occurs only above the "limit kappa number" value⁶. Moreover, the use of this oxygen process only decreases the chlorine demand of the pulp without eliminating the use of chlorine.

We demonstrated⁹ in 1979 that pretreatment at 100°C during one hour of the alkaline wood pulp (kraft and soda/AQ) with a dilute sulfuric acid solution (N/65) led to a more thorough oxygen delignification (kappa number ~3), without excessive degradation of polysaccharides (viscosity $(\eta) > 760$ ml/g). Abrahamsson and Samuelson¹⁰ used a NO_2/O_2 -pretreatment of the pulp at 56°C and obtained a smaller but significant improvement in oxygen delignification without excessive degradation of the polysaccharides. Lachenaud and de Choudent¹¹ observed the same improvement with a Cl_2 -pretreatment of the pulp at 70°C. Fossum and Marklund¹² reported similar improvements when pretreating the pulp either by ClO_2 at 50°C or by H_2O_2 in an acid medium at 60°C. When pretreating a kraft wood pulp at 70°C by dilute H_2SO_4 (N/22) Gellersiehl and Lindfors¹³ obtained a slight decrease in kappa number.

All of these pretreatments are performed in an acid medium at an elevated temperature and we can observe that the bleaching processes of the alkaline wood pulps nowadays make use of a hot acidic stage. The aim of our study is to elucidate the role of the acid medium at about 100°C on an alkaline-wood pulp (kraft or soda/AQ) in view of further bleaching by oxygenated compounds.

MATERIALS AND METHODS

Methods of Analysis

Pulp properties were determined according to appropriate standard procedures.

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Pulp yield was always determined by weight (o.d.) loss, after pulp washing by running water on a wire mesh (mesh opening: 90 μm) and air drying.

UV absorption: after suitable dilution with distilled water, the absorbance was determined at pH=11 by NaOH addition. The absorbance at 245 nm were calculated for the undiluted liquor on the assumption that the absorbance was directly proportional to the solute concentration.

HPLC used a MERCK "ODAV" column (solvent: H_2SO_4 N/100, flow rate: 0.5 ml/min., column temperature: 35°C).

^1H and ^{13}C NMR analysis carried out in "Leningrad S.M.Kirov Forest Technical Academy".

Acidification of the Suspensions

An anhydrous mass, ml, of air-dried fibers was defiberized with a domestic mixer, with 800 g of distilled water (1 distillation, ρ : 0.997 g/cm³, pH: 5.62). Known acid volumes (~1N) were added to the suspension with a microburette at room temperature (~23°C). After each acid addition, the suspension was agitated for two minutes with a magnetic stirrer. The stirring was stopped and the pH was measured with pH-probes dipped directly into the suspension for three to ten minutes until a constant value was obtained.

Kinetic Study of the Hydrolysis Stage (A)

A 20 g anhydrous mass of air-dried fibers was defiberized with a known quantity of liquor (about 800 ml) in a 1.5 litre stainless steel rotating autoclave, electrically heated. The temperature was increased 3°C per minute. The pH and absorbance measurements were done on successive samples of liquor filtered on a sintered glass crucible (porosity < 5 μm) and frozen.

The buffer solution was made by adding NaOH into a NaHSO_4 0.4M-solution until a measurement of pH ~ 2 was obtained.

Bleaching of the Products dissolved by dilute H_2SO_4 -Hydrolysis

A 455 g anhydrous mass of air-dried soda/AQ pulp of *carpinus betulus* (kappa number: 24.8, viscosity (η): 930 ml/g) was mixed in 18 litres of distilled water previously acidified with H_2SO_4 up to pH=2. After defiberizing the pulp was

transferred into a twenty-liter stainless steel extractor, the pH of the suspension was equal to 2.18. The suspension was slowly stirred and heated by a water jacket. It took about 40 minutes to reach 95-100°C.

The absorbance at 245 nm of the liquor was 15.0 after two hours at 95-100°C. The hydrolysis was stopped effectively after three hours. After this treatment the yield=96.4%, the kappa number=16.4 and the viscosity (η)=760 ml/g.

The separated liquor (14.8 litres) was filtered on a sintered glass crucible (porosity < 3 μ m) and neutralized to pH=7 by adding NaOH and then concentrated to 350 ml by evaporation at 50°C under reduced pressure (water respirator). These 350 ml were H₂SO₄ acidified to pH=1.8 and continuously extracted by chloroform. The chloroform extract was evaporated to dryness at 50°C and analysed.

RESULTS AND DISCUSSION

Influence of Pulp Acid Hydrolysis on Further Oxygen Bleaching

We started previously⁹ with alkaline (soda/AQ, kraft/AQ and kraft) hardwood pulps of *carpinus betulus* obtained by cooking at 138°C. Those pulps were hydrolysed by dilute sulfuric acid (N/65) before oxygen bleaching. The same method is used but with a cooking temperature of 165°C. The conditions and the results of which are presented in TABLE 1.

Air-dried pulp samples I and II are treated according to, either an acid hydrolysis stage (A) or an oxygen bleaching stage (O), or the two stages in the order of the symbols A and O. A washing with running water on wire mesh is done between each stage. For instance, IOA is for sample I which is first hydrolysed (A), washed, and bleached with the oxygen process (O). The conditions for these treatments are presented in TABLE 2 and the results in TABLE 3.

As compared with a first study⁹, we find again the same improvement in delignification (kappa number) without excessive degradation of the polysaccharides (viscosity (η) > 760 ml/g). As shown by de Choudens, Lachetel et al¹⁴, the hot acid washing of the pulp, which eliminates the heavy metal ions, improves hydrogen peroxide delignification. Moreover, they observed that raising the temperature in the acid treatment further decreased the kappa number after the H₂O₂ stage even though the metal ion content of the pulp was not altered. These authors concluded that "a significant amount of β -ether linkages were left unhydrolysed during kraft pulping

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TABLE 1
Soda/AQ: Cooking of air-dried *Carpinus betulus* Wood Chips.

Experiment	I	II
NaOH, g / 100g o.d. wood	20	20
Anterquinone, g / 100g o.d. wood	0.5	0.5
Liquor-to-wood ratio, l/kg o.d. wood	3.5	3.5
Time to temperature, min.	90	30
Time at 165°C, min.	30	30
Pulp yield, % of o.d. wood	50.1	30.7
Kappa number	20.1	23.1
Viscosity int. ml/g	888	949

TABLE 2
Conditions for the Oxygen Bleaching Stage (O) and the Hydrolysing Stage (A).

Oxygen Bleaching Stage (O)	Hydrolysing Stage (A)
NaOH, g / 100g o.d. pulp	H ₂ SO ₄ , g / 100g o.d. pulp
Consistency, % in weight	Consistency, % in weight
Oxygen, MPa at room temperature	Time to temperature, min.
Total Pressure at 115°C, MPa	Time at 101°C, min.
Protector (Mg ²⁺ salt)	
Time to temperature, min.	
Time at 115°C, min.	

TABLE 3

Analysis of Pulpas I and II after the Treatments performed in the Order of the Symbols O and A.

Sequence nature	Final pulp yield % o.d. wood	Kappa number	Viscosity int. ml/g	g formal / 100g o.d. wood
I	50.1	20.1	888	7.55
IA	47.0	11.7	850	6.72
IAO	44.3	3.2	787	6.30
IO	43.6	9.4	767	6.38
IOA	43.3	2.6	779	6.38
II	50.7	23.1	949	7.57
IIA	47.4	15.6	810	-
IIAO	44.7	4.2	-	-
IIO	46.6	9.8	-	-
IIOA	44.1	3.2	-	-

alkaline
pulp

high
viscosity

He or

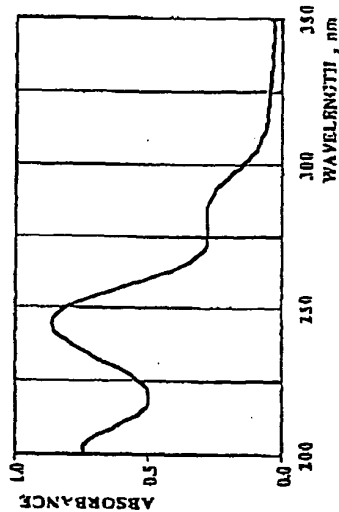


FIGURE 1. UV Spectrum of the hydrolysis Liquors corresponding to Treatment Sequences 1A and 10A as quoted in TABLE 3; the two Spectra were identical.

and were cleaved by acidolysing the lignin, consequently formation of carbonyl groups along with release of free phenolic groups was achieved¹⁵, that favours the dissolution of the lignin during the following H_2O_2 -treatment¹⁵.

Our results in TABLE 3 show: -first, the improvement (as measured by kappa number) of the delignification is obtained not only during the oxygen treatment but also during the acid treatment; -second, the kappa number decrease due to the acid treatment alone is about same order whether the hydrolysing stage is done before or after the oxygen treatment (Δ kappa number ~ 7), so this improvement seems specific to the acid treatment of the pulp.

Therefore, it appears that the third part of the residual oxidizable materials (lignin?) in our pulp obtained after the alkaline cooking, can be dissolved during the acid hydrolysis of the pulp alone, when performed at about $100^\circ C$. This assumption is confirmed by UV spectra analysis in the wavelength range 200-350 nm (FIGURE 1) which was done on the hydrolysis liquors: two maxima of absorbance appeared at 245 nm and 285 nm, which are characteristic of a carbonyl group on the side chain of a guaiacyl unit^{16,17}.

As our measurements of the furfural index (TABLE 3) showed that the hemicelluloses were not significantly dissolved during this hydrolysis stage, as compared to the oxygen treatment alone, i.e. 1AO and 10A to 10, consequently we

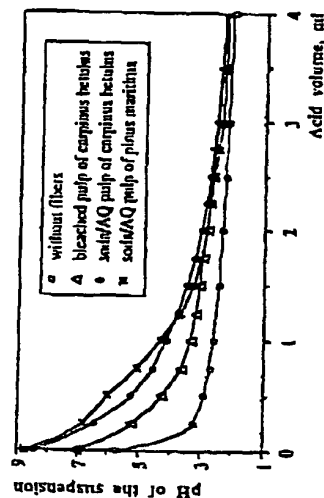


FIGURE 2. Acidification by 1.005N H_2SO_4 at room Temperature of 800g distilled Water containing 10.12g (o.d.) of air-dried Pulp.

were searching for the nature of the dissolved products. In a first step, a kinetic study of acid hydrolysis is necessary in order to know its main parameters.

Study of the Acidification of Alkaline Wood Pulp Suspensions

In principle, the acid hydrolysis of the pulp can be related to the H^+ concentration of the suspension, but as the wood fibers behave like cation exchangers¹⁸, the pH of a suspension depends on:

- the quantity of acid introduced,
- the initial anhydrous fiber mass,
- the pulp consistency.

Thus, we have studied the acidification of alkaline wood pulp suspensions according to experimental conditions which are as close as possible to our hydrolysis stage.

For a consistency of 1.25%, we tested four different strong acids: HCl, $HClO_4$, HNO_3 , H_2SO_4 . We did not observe any difference in behaviour with respect to the anion nature for the pH-range (initial to pH=2) studied.

In the same way, with HNO_3 , no differences were observed with soda/AQ *carpinus betulus* pulps at 110, 68, 31.5 and 21 kappa numbers. However, the same experiment performed with a bleached *carpinus betulus* pulp (FIGURE 2)

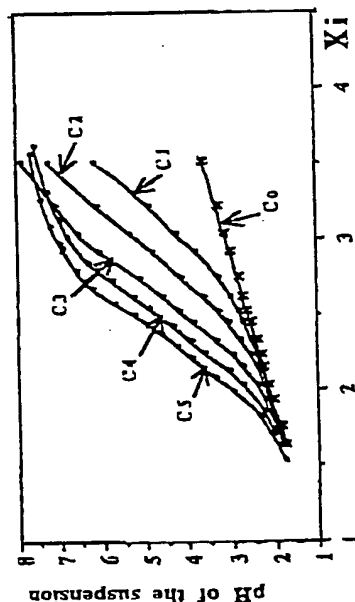


FIGURE 3. Measured pH of the Suspension of unbleached Soda/AQ *Corpinus betulus* Pulp as a function of X_i , i.e. the Logarithm of the calculated H^+ Concentration, for several initial Pulp Consistencies: $C_0=0$ (distilled Water); $C_1=0.63\%$; $C_2=1.25\%$; $C_3=2.47\%$; $C_4=3.67\%$; $C_5=4.84\%$.

showed a lesser H^+ adsorption as compared with unbleached pulp, results which are in agreement with the fact that the last laboratory bleaching stage (CEDED) was done in a buffered suspension (pH=4.8) and that the bleached pulp had a lower total carboxyl value than the unbleached pulp¹⁹.

FIGURE 3 shows the results obtained with 0.944N HNO_3 and several consistencies: we present our measured pH-values as a function of X_i , i.e. the logarithm of the calculated H^+ concentration.

The electrokinetic properties of the fiber suspensions have been extensively studied²⁰ and we have chosen to exploit our results according to the model proposed by Grignon and Scallan²¹, in which the measured mean water retention value is 1.5 g of water per 1g of anhydrous kraft wood pulp, in a wide range of pH-values.

Assuming that equilibrium is reached between the gel phase (i.e. the solution inside the fiber wall) and the external liquid phase (i.e. the solution outside the fibers), the amount of H^+ adsorbed by the fibers is estimated and presented in FIGURE 4.

We observed that the adsorbed H^+ quantity is a function of consistency and the pH measured and reaches a broad maximum for a constant consistency. Our results

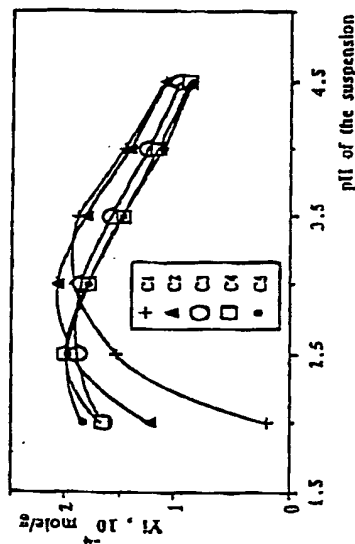


FIGURE 4. Calculated Mole Number of H^+ adsorbed per 1g of anhydrous Fibers, Y_i , as a function of the measured pH of the Suspension for several initial Pulp Consistencies: $C_1=0.63\%$; $C_2=1.25\%$; $C_3=2.47\%$; $C_4=3.67\%$; $C_5=4.84\%$.

are in agreement with the model proposed by Grignon and Scallan. The pulp in our experiment was not previously delonized by acid washing and, thus, the increase of the pulp consistency leads to an increase of the salt concentration in the solution. In accordance with the conclusion of these authors, we observed the translation of the H^+ adsorption curves towards lower pH-values when the salt concentration increases. Thus the pH-difference between the solution inside the fibers and the external solution is reduced by an increase in pulp consistency. The curves in FIGURE 4 are only slightly translated along the Y axis for the high consistencies by the value used for the constant water retention value.

Our method is suitable only for pulp consistencies <5% and could be more rigorous by measuring the pH of the external liquid phase before and after separating the fibers by filtration to ascertain that equilibrium was reached between the external liquid and the gel phase. Moreover, the water retention values of our pulp should be determined with respect to the pH.

However, the small water retention value variations registered, by Orignon and Scallan²¹ between pH=7 and pH=2 and by Lindström and Carlsson²² between pH=7 and pH=4, for unbleached kraft wood pulps, added to the fact that our pulp consistency is lower than 5%, make it possible to consider that our approach is

TABLE 4

Hydrolysis of unbleached (kappa number: 20.0; η): 979 ml/g) Kraft pulp of *Carpius betulus*.

Hydrolysing medium	Buffer	Buffer	1.50 ₄	H ₂ O
pH of the suspension before hydrolysis	2.10	1.96	1.98	4.13
Hydrolysis temperature, °C	110	103	88	110
Total hydrolysis time, min.	90	150	300	90
Total Q, litre	7.80	8.33	7.38	9.36
Final pH of the suspension	2.09	1.93	1.96	3.73
Pulp yield, % of o.d. pulp	94.1	96.2	95.8	93.4
Kappa number	12.1	12.8	13.5	12.2
Viscosity η , ml/g	926	972	1024	934
				1009

reliable. Taking into account the shape of the curves in FIGURE 4, we believe, as Grignon and Seillon have suggested, that a main parameter of the considered hydrolysis stage (A) is the H^+ concentration in the gel phase. The existence of a broad maximum for the adsorbed H^+ quantity makes it possible to control the H^+ activity, i.e. the H^+ concentration in the gel phase for a constant water retention value, either by putting a buffer solution in the suspension, or by acidifying the suspension up to a measured pH in the external liquid phase that is included within the boundary lines of the adsorption plateau.

Kinetic Study of the Hydrolysis Stage (A)

The kinetic study was performed by following the absorbance of the liquor between $\lambda=225$ nm and $\lambda=245$ nm as a function of hydrolysis time. The results obtained for $\lambda=245$ nm are presented in TABLE 4 and on FIGURE 5 where Q, determined by multiplying the absorbance at 245 nm by the volume of the hydrolysis liquor, was corrected with the values obtained for the successive samples of removed liquor.

On FIGURE 5, the Q-values different from zero obtained with H_2O , do not correspond to a maximum of absorbance at 245 nm which was specific to the extracted products when the suspension was acidified before treatment; in fact, the product(s) of the acid hydrolysis reactions were not extracted by auto-hydrolysis with water in our operating conditions; however, the auto-hydrolysis extracted products had a non zero absorbance value at 245 nm and the conventional

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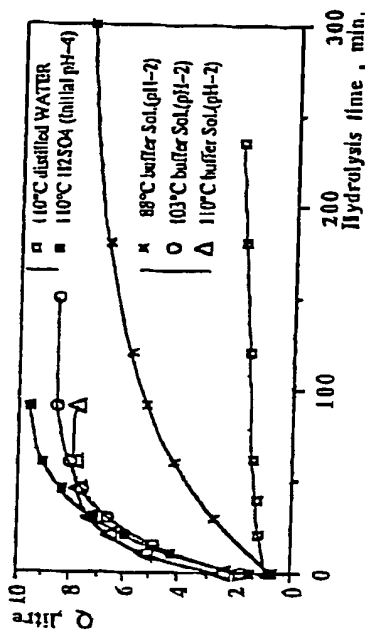


FIGURE 5. Kinetic Study of acid Hydrolysis of unbleached Kraft Pulp of *Carpius betulus*. Q, is related to the Quantity of extracted Products.

exploitation of these results as kinetics parameters was not possible because we could not assume that the reactions during auto-hydrolysis were independent of the pH-value.

From FIGURE 5, we can determine the initial extraction rates for the three temperatures studied and as a first approximation their relative values would be 1:2:3 at 90°C, 100°C, 110°C respectively.

A second kinetic study at 103°C was performed with the air-dried pulp obtained after the first series of measurements (yield, kappa number, viscosity): the characteristic spectrum, as shown in FIGURE 1, was no longer reproduced; after 135 minutes at 103°C, the absorbance at 245 nm = 0.675, the yield of new hydrolysis = 96.3%, the kappa number = 11.8 and the viscosity (η) = 873 ml/g. This second hydrolysis of an already hydrolysed sample shows that the first extraction was complete and, moreover, we can evaluate the degradation of polysaccharides at 103°C in our operating conditions: $\Delta(\eta) = 0.75$ ml/g per minute of hydrolysis, this order of magnitude is the same when calculating from results in TABLE 3.

The results from dilute H_2SO_4 hydrolysis at 110°C, with H^+ concentration in the external liquid phase 100 times lower (pH=4) than the one used with a buffer solution (pH=2), but with a theoretical adsorbed H^+ quantity per gram of anhydrous fibers equivalent (-1.5×10^{-4} mole/g) validate our assumptions to

Interpret the acidification of the pulp suspensions and confirm the shape of the curves on FIGURE 4.

Some viscosity values in TABLE 4 are higher than the initial values obtained for the pulp before hydrolysis, these values have been confirmed by new determinations and are not yet explained.

This kinetic study shows nevertheless that the extraction efficiency of the *corpius brunus* pulp can be obtained in an open reactor at temperatures between 90°C and 100°C. The necessary acid quantity depends on the pulp consistency but, owing to the existence of an adsorption plateau for the H^+ adsorption in the gel phase, in practice, this acid quantity will be added before hydrolysis until the measured pH of the suspension is included in the range 2-3.5 and for a pulp consistency in the range 2.5%-5%. Once these conditions were fixed, we checked the extraction by absorbance measurements in the range $\lambda=225-225nm$ on samples which were taken from the liquor.

Analysis of the Products dissolved by dilute H_2SO_4 Hydrolysis

After pulp hydrolysis and chloroform extraction of the hydrolysis liquor according to the description in the MATERIALS AND METHODS section, the chloroform extracted material was analysed by 1H NMR (50 MHz, acetone- d_6 , $\delta(ppm)$: 6.62, 7.22, 7.79, 9.80) and ^{13}C NMR (200 MHz, $CDCl_3$, $\delta(ppm)$: 112.3, 120.0, 144.0, 147.5, 163.4).

This material was mainly 2-furancarboxylic acid (2-FCA), the purity of which can be evaluated by comparison of infrared spectra (A) and (B) in FIGURE 6.

The UV spectrum (FIGURE 7) of the products not extracted by chloroform revealed the absence of a maximum absorbance at $\lambda=245 nm$ and consequently the 2-FCA was alone responsible for this maximum absorbance²³ in FIGURE 1. At the beginning of this study, this acid had been mistaken for an aromatic compound because of a similar spectrum. The extracted 2-FCA quantity was more than 0.5g per 100 g of anhydrous pulp mass.

Is the 2-FCA responsible for the existence of a "limit kappa number" when performing oxygen bleaching?

To give a response, a mixture of IO and IIO pulp (TABLE 3) was hydrolysed by dilute sulfuric acid at 110°C and at initial pH of the suspension 2.38. A similar kinetic study as precedingly was performed: after 45 minutes the maximum of

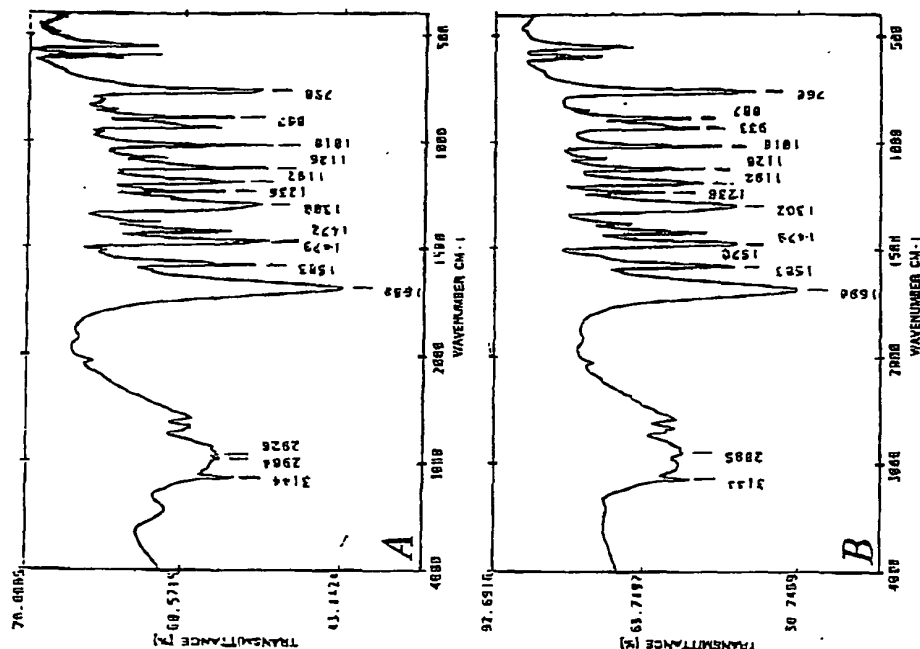


FIGURE 6. Analysis of the dissolved Products during dilute H_2SO_4 Hydrolysis:
(A) : FTIR Spectrum of the Extracted Material by Chloroform.
(B) : FTIR Spectrum of 2-Furancarboxylic Acid (Purity 98%).

2.38

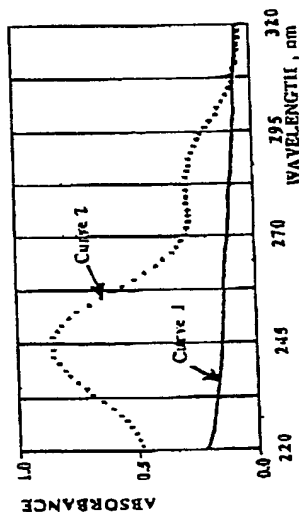


FIGURE 7. Analysis of the dissolved products during dilute H_2SO_4 hydrolysis: Curve 1: UV Spectrum of the Remaining Hydrolysis Liquor after Extraction by Chloroform - Curve 2: as in FIGURE 1.

absorbance at 245 nm of the liquor became stable; $Q=8.54$ litres (FIGURE 5). In an independent experiment, when oxidizing the 2-FCA by $KMnO_4$ in the usual conditions of the kappa number measurement, we observed that the kappa number was in correlation with the 2-FCA quantity: $\text{gram 2-FCA} / 100\text{g (o.d.) pulp} = 0.23 \text{ kappa number}$.

These results and those in TABLE 3 show the relation which exists between the kappa number reduction and the appearance of 2-FCA in the acid hydrolysis liquors. The "limit kappa number" observed in the oxygen bleaching would be due to the presence in the unbleached *carpinus betulus* pulp of materials which can release 2-FCA in acid medium and which are not oxidized during oxygen bleaching.

The treatment in acid medium of alkaline wood pulps is known to decrease the physical properties of the manufactured papers, essentially the tear index. To evaluate the impact of the acid extraction in this work we refined our original 455g of pulp which had been extracted by hydrolysis in a valley beater. The physical characteristics are presented in TABLE 5 and can be compared with both those from the same soda/AQ pulp of *carpinus betulus*, but after bleaching, and those from a bleached kraft pulp of *carpinus betulus*. (The bleaching process in the two cases was a classical laboratory bleaching CEDED).

TABLE 5

Properties of chemical Wood Pulps of *Carpinus betulus* after refining in a Valley Beater.
A: Soda/AQ Pulp hydrolysed with dilute H_2SO_4 (original 455g).
B: Soda/AQ Pulp bleached with classical Laboratory CEDED-Sequence.
C: Kraft Pulp bleached with classical Laboratory CEDED-Sequence.

Pulp Type	A	A	A	B	B	C	C
(1) Refining Time, min.	0	18	19	0	63	0	58
Shopper-Riegler Process, °SR	21	60	72	15	68	18	65
Water Retention Value, g/g.100	137	178	229	116	201	112	207
Bauer-McNett classification, wt. %							
33-mesh	60.8	59.7	47.4	49.4	26.1	47.5	27.0
63-mesh	21.2	16.5	24.0	28.1	21.6	33.3	20.0
100-mesh	5.3	5.8	5.7	3.7	12.0	7.0	17.5
150-mesh	2.3	3.8	4.1	1.4	7.2	2.0	10.0
passed 150-mesh	10.4	14.2	18.8	13.4	33.1	10.0	15.5
Bulk, cm ³ /g	1.73	1.22	0.98	1.90	1.24	1.95	1.26
Zero-span tensile, LRo(wet), m	9100	7900	3600	12150	9500	10050	9350
Zero-span tensile, LRo(dry), m	17300	12300	12600	12680	14700	11870	13900
Breaking length, LR, m	3700	7300	7600	2170	9160	2000	6930
(LR/LRo(dry)) 1.00	30.0	56.4	60.0	17.1	54.2	16.8	50.0
Burst index, mPa.m ² /g	2.40	4.50	4.10	1.23	4.35	1.79	4.92
Tear index, mN.m ² /g	4.90	5.10	4.60	10.24	10.15	9.30	7.93
Double fold (455g), number
Double fold (700g), number	21	310	570

(5) The refining time corresponds to the application time of the movable weight on the bedplate lower arm of the valley beater which goes on when the movable weight is removed.

The first remark deals with the high refining rate of the hydrolysed pulp: 18 minutes are necessary to obtain °SR: 23 for the reference kraft or soda/AQ pulps, which explains our lack of measurements between °SR: 21 and °SR: 60.

The Bauer-McNett classification, show a cut of the fibers much less significant than for the reference pulps, higher values of the WRV and of the ratio LR/LRo, overall evidence of the highest hydration capacity for the hydrolysed pulp and consequently a better aptitude for refining; however, the two conclusions should be certified by appropriate microscopic studies of the pulp during refining.

As expected the tear index was largely decreased, the burst index and the breaking length were the same, meanwhile the double fold was clearly improved: it was necessary to increase the weight of the load from 450g to 700g to obtain the break of the test piece before excessive duration.

As the hydrolysis parameters were chosen to study conveniently the nature of the dissolved products, the measured physical characteristics were probably not the best; in fact, taking into account the kinetic study results, we can suppose that an

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